INTRODUCTION

With intensive development of advanced technologies, such as electronics and solar energy, pure silicon becomes an important material for the industry, and the demand on this product is constantly rising. On the industrial scale, silicon is typically produced by the reduction of silicon dioxide with carbon in high-temperature furnaces [1]. However, this method is energy consuming and requires relatively long processing time. The investigations are still going on to improve this process [2, 3]. Also, the final product usually should be subjected to additional purification. Moreover, the main by-product of this technology is carbon dioxide responsible for the undesired greenhouse effect. Attractive “green” approach to silicon and silicon nitride production based on using the solar energy was suggested in [4]. But this process requires a lot of time and thus is ineffective. Two other similar methods for silicon production, aluminothermy and magnesium reduction are also well known. The former one leads to the formation of alumina which is a chemically stable phase and thus the process of silicon purification is difficult and expensive. The latter one, i.e. conventional magnesium-reduction method, is more efficient [5–7]. However, this energy consuming and long-term heat treatment approach does not afford production of submicron powders.

In this work, we explored the synthetic routes to production of high surface area silicon nanopowders by SHS method [8, 9] being attracted by its simplicity, essentially zero energy consumption, and uniqueness of product characteristics. Microstructural analysis of the powders synthesized from different raw materials allowed us to suggest the mechanism of structural transformations taking place in the combustion wave. Based on this mechanism, an effective approach to controlling the microstructure of final product was proposed.

EXPERIMENTAL

For a stoichiometric composition (Mg : SiO₂ = 2 : 1), the overall SHS reaction can be written as follows:

\[ \text{SiO}_2 + 2\text{Mg} = \text{Si} + 2\text{MgO}. \]

The results of thermodynamic calculations for the adiabatic combustion temperature \( T_{ad} \) and amount of equilibrium products as a function of inert gas (Ar) pressure \( P_{in} \) in the reactor are shown in Fig. 1. It can be seen (Fig. 1a) that when \( P_{in} \) increases, \( T_{ad} \) also increases while the amount of gas-phase products, such as Mg(g) and SiO(g), decreases. This effect can be explained by the fact that high \( P_{in} \) “suppresses” gas phase formation, thus leading to an increase in \( T_{ad} \). Note, that in the range of \( P_{in} = 1–20 \text{ atm} \), the values of \( T_{ad} \) (2100–2200 K) are well above the melting points (m.p.) of magnesium (922 K), silicon (1683 K), and silicon oxide (1923 K) as well as the boiling point (b.p.) of Mg (1363 K), but below the m.p. of magnesium oxide (3073 K). Finally, while \( P_{in} \) increases, the amount of undesirable Mg₅Si₄O decreases (Fig. 1b) giving almost 99.999% pure silicon.

Magnesium (Mg) powder from Alfa Aesar, USA (99.8% purity, mean particle size \( d \leq 44 \mu m \)) was used in all experiments. Three different types of silicon oxide (SiO₂) powder were used: (i) from the Yerken deposit, Kazakhstan, marked hereinafter as KZ (98.8% purity, \( d \leq 100 \mu m \)), (ii) from Cerac, WI, USA, marked as Cerac (99.5%, \( d \leq 44 \mu m \)); and (iii) from Cabot Corporation, USA, nano Untreated Fumed Silica marked as UFC (99.9%, BET ≈ 200 m²/g). Typ-

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1 The text was submitted by the authors in English.
COMBUSTION SYNTHESIS OF SILICON NANOPowDERS

Fig. 1. Thermodynamic characteristics as a function of inert gas pressure $P_{in}$: (a) adiabatic combustion temperature $T_{ad}$ and total amount of gaseous products; (b) equilibrium amounts of condensed products.

Fig. 2. Chemical microstructures of these SiO$_2$ powders are presented in Fig. 2.

Starting reactants were thoroughly mixed in desired ratios and compacted in an automatic press-plant (Carver, Inc., USA) into cylindrical samples (10, 30, 40 mm in diameter and 25–50 mm long) with a relative density of up to 70%. Thus prepared samples were horizontally placed onto a graphite tray and inserted into a cylindrical steel reactor with transparent windows for monitoring the process. The reactor was evacuated to $10^{-3}$ atm and then filled with argon up to 1–20 atm. Ignition was carried out by passing a short (<5 s) dc pulse ($I = 10$ A, $U = 20$ V) through a tungsten wire located close to the sample surface.

All synthesized samples were leached for 3 h with 36% hydrochloric acid under normal conditions (without any additional heating). The acid was taken according to the amount of magnesium oxide in as-synthesized product at a 1 : 1 ratio [10]. The samples were dried at normal conditions for about 10 h and then subjected to analysis.

A digital video camera (model DCR-DVD301, Sony Electronics), a pyrometer (Model 100C, Luxtron Corp. CA), and 50-μm W–Re thermocouples were used for measuring combustion wave velocity and temperature-time history. Microstructures of synthesized powders and their elemental/phase compositions were examined by FESEM (Magellan 4000, FEI), EDS (INCAx-sight Model 7636, Oxford Instruments, Concord, MA), and XRD (Scintag, X1...